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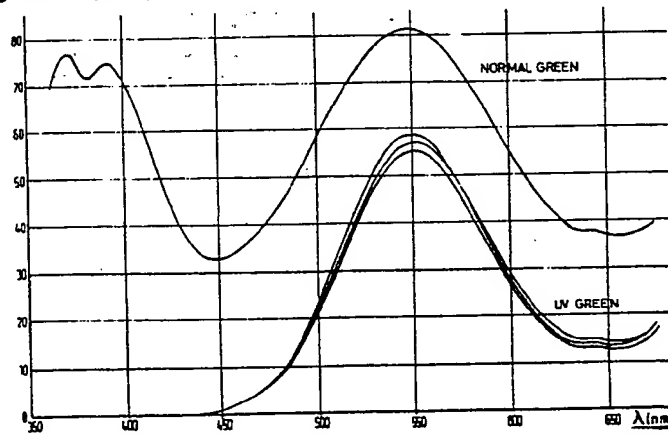
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(54) A process for producing a UV-absorbing green glass.

(57) The invention concerns a process for making green glass permeable to visible light and highly absorbing to ultraviolet radiation, by treating a melt of a soda-lime glass under oxidizing conditions with a gas, said melt containing chromium compounds and nitrate.

In order to be able to use recycle glass, more in particular containing iron contamination, the invention is characterized by blowing an oxidizing gas into the melt of the glass, which contains at least 0.3% by weight of chromium, calculated as Cr_2O_3 , 0.2-2.0% by weight of Na nitrate, no more than 1.5% by weight of Na sulphate, and 15 to 65% by weight of recycle glass.



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A process for producing a UV-absorbing green glass

The present invention relates to a process for producing a UV-absorbing green glass that is permeable to visible light and highly absorbent to ultraviolet radiation, which glass is suitable for the manufacture of containers for products sensitive to UV radiation, by treating a glass melt in a tank furnace with a gas blown into the furnace through nozzles.

5 French patent 1,275,824 discloses a process for making a UV-absorbing green glass by oxidizing trivalent chromium compounds in the glass melt to hexavalent chromium in the presence of Na nitrate.

UV-absorbing glasses are used, among other purposes, for the manufacture of containers for light-sensitive products. Examples of undesirable photochemical reactions caused by short-wave light, in particular UV radiation, are deterioration in flavour in the case of beer, wine and soft drinks, rancidification of
10 oils, and loss of vitamins, for example, in milk.

The light-induced deterioration in the quality of beer is known from "Untersuchungen zur Lichtdurchlässigkeit von Flaschen, Gläsern und deren Bedeutung für die Qualitätserhaltung von Bier", Heinrich Vogelpohl, Weihenstephan, July 1981, pp. 44-50. According to this publication, radiation between 300 and 500 nm, i.e. partially UV radiation and partially visible light, is harmful to beer.

15 In order to prevent, or at any rate reduce, such undesirable reactions induced by light, it is known to use containers, for example bottles, made of brown or amber-coloured glass. Such glasses, however, have the disadvantage that, with a sufficient absorption of UV radiation, their transparency is relatively low, so that a visual observation and inspection of the product is difficult, if not downright impossible. The use of green glass for packing beverages, therefore, has a sales-promoting effect.

20 The use of green glass to protect UV-radiation sensitive products is also known. From "Colour Generation and Control in Glass", C.R. Bamford, 1977, page 46, it is further known that chromium-containing green glass is highly absorbing in the short-wave range of the spectrum, and that, for attunement between permeability in the visible range and absorption in the ultraviolet range, the ratio between trivalent and hexavalent chromium is of particular importance. Hexavalent chromium will absorb more in the UV
25 range and trivalent chromium in the visible range.

On the basis of fundamental knowledge about the effect of chromium and its valency on the absorption characteristics in the visible and ultraviolet ranges, various glasses and process for their preparation have been proposed. Indeed, the basic starting point is that, to achieve a sufficiently high degree of oxidation to convert trivalent chromium oxide to hexavalent chromium oxide, the iron content should be kept as low as
30 possible. This is only possible by using expensive starting materials poor in iron, and by avoiding impurities which may be caused, for example, by recycling glass. See for example the article by Güldal and Apak "A study on $\text{Cr}^{3+}/\text{Cr}^{6+}$ Equilibria in Industrial Emerald Green Glasses, Journal of Non-Crystalline Solids 39 & 39 (1980), 251-256.

35 The object of the present invention is to provide a process for preparing UV-absorbing green glass, which glass exhibits UV-absorption in the range below 500 nm comparable to brown glass, but which process in addition makes possible the use of inexpensive starting materials, specifically those having high iron contents and many impurities, such as recycling glass.

According to the present invention, this object is achieved by blowing an oxidizing gas into the melt of the glass which glass contains at least 0.3% by weight of chromium, calculated as Cr_2O_3 , 0.2-2.0% by
40 weight of Na nitrate, no more than 1.5% by weight of Na sulphate, and 15 to 65% by weight of recycle glass.

Advantageously, as will be indicated further hereinafter, the oxidizing gas used in the process according to the present invention is technically pure oxygen, or air enriched in oxygen. Specifically, the content of molecular oxygen is more than 50 or 95% by volume.

45 According to the present invention, it has been found to be possible to limit the amount of added chromium compounds without detracting from the UV-absorbing effect, if the amount of fluorine and chloride in the starting products is minimized. This can be accomplished by starting from soda with a low chloride content (0.2% by weight), not adding fluorspar (a source of fluorine), and avoiding plastic-coated recycle glass (PVC source) as much as possible.

50 Preferably, the content of fluorine and chloride is each restricted to maximum 0.01% by weight, preferably maximum 0.001% by weight. Limiting the amount of chromium in the glass has two advantages. First chromium-containing raw materials are expensive, so that a limitation of the chromium content is advantageous, and second glass with a high chromium content is difficult to re-use.

Advantageously, the starting product in the process according to the present invention is a mixture of the following starting products (in kg, calculated on 1000 kg glass mixture):

	sand	300-400 kg
5	soda	50-150 kg
	limestone	60-105 kg
	dolomite	0-25 kg
	phonolite	0-40 kg
	feldspar	0-45 kg
10	chromium ore	0-15 kg
	chromium oxide	0-5 kg
	chromium slag	0-70 kg
	sodium sulphate	0-11 kg
	nitrate	4-15 kg
15	fragments	350-586 kg

with at least one of the quantities of chromium ore, chromium oxide and chromium slag not being zero.

According to the present invention there is thus produced a glass having the following composition (in % by weight):

	SiO ₂	70-74 % by weight
20	Al ₂ O ₃	1.5-2.5 % by weight
	Fe ₂ O ₃	0.25-0.7 % by weight
	chromium oxide	0.3-0.85 % by weight (as Cr ₂ O ₃)
	CaO	10-11 % by weight
	MgO	1-2 % by weight
25	Na ₂ O	12-14 % by weight
	K ₂ O	0.4-1 % by weight
	SO ₂	0.1-0.3 % by weight.

The combination of the starting materials used according to the invention, the introduction of an oxidizing gas, preferably oxygen, surprisingly gives the following advantages:

- 30 1. sufficient oxidation of the organic impurities of the fragments used, as will be further elaborated hereinafter;
2. shift of the Fe-II/Fe-III ratio to higher values, which also affects colour and heat absorption;
3. improvement of refinement;
4. reduction of rejects as a result of silicon inclusions; and
- 35 5. increase of the melting capacity by about 5%.

The varying amounts and kind of organic impurities introduced by the fragments (recycle glass) and starting materials lead to a continuously changing reduction potential. The resulting required changes of the redox potential of the melt result in deterioration in quality (changes in heat absorption resulting from varying IR transmission, varying degassing conditions). The oxidation of the impurities by the oxidizing gas, 40 such as oxygen, provides the basis for a particularly constant redox potential of the melt.

In the case of green glass, the colour of the glass, and also the IR transmission, are greatly influenced by the degree of oxidation of the melt. The use of oxygen makes for easy and exact control within a specific band width.

The green glass obtained by using the process according to the present invention has a dominant 45 wavelength (λ dominant) which may be in the vicinity of 550-565 nm.

The presence of trivalent chromium, in combination with possibly other coloured compounds that may be present, determines the exact dominant wavelength. When Cr₂O₃ is partially replaced by up to 0.2% by weight of nickel oxide, the colour is shifted to olive green. The other characteristics of the glass, however, are not thereby changed.

50 The permeability to infrared radiation in the range of the Fe²⁺ band is increased by about 20-30%. The increased permeability to infrared radiation leads to an improved heat absorption by the glass melt.

The use of oxygen as an oxidizing gas instead of air gives a clear improvement in refinement. The oxygen is preferably substantially free from impurities, i.e., its content of molecular oxygen is more than 95% by volume. It is also possible, however, to use oxygen with a higher content of inert gases, for 55 example, oxygen containing at least 50% by volume of molecular oxygen. By using pure oxygen, the number of gas bubbles with a diameter less than 1 mm on average was reduced from 1.8 to 0.7/g glass, and particularly the larger diameter bubbles disappeared. This is a considerable improvement in glass quality.

Preferably, in addition to the saltpetre or Na nitrate, a minor proportion of sodium sulphate is used, for example, minimum 1 kg per 1000 kg of glass batch. This has a particularly favourable effect on the number of bubbles. High proportions of sulphate, as often used according to the state of the art (10-20 kg 1000 kg glass batch) are preferably not used, because this leads to a great increase in foaming, which has an adverse effect on heat transmission.

The manufacture of the glass takes place at conventional temperatures such as 1400 to 1500°C.

As, in the case of soda lime glass, the larger gas bubbles in the melt, prior to refinement, often contain CO₂, N₂ and H₂O, oxygen as a refinement gas is particularly effective. In fact, in this case the difference in concentration between the melt and the gas bubbles is largest. There is then a diffusion of the refinement gas (in this case O₂ and SO₂) to the bubbles, as a result of which these become larger as the temperature is increased, and escape from the melt. When the temperature is decreased (for example, in the tank furnace and the supply chute) the gas bubbles are diffused back into the melt, which leads to a resorption of, particularly, the small gas bubbles.

When fragments, i.e. recycle glass contaminated with aluminium (capsules, foils) are used, there is the danger of the reduction of silicon dioxide (SiO₂) by aluminium to elemental silicon, which separates in the glass in the form of compact spheres. On account of the large difference in coefficient of expansion of glass, on the one hand, and silicon, on the other, high compressive stresses are present in the glass after cooling which lead to breakage right away, or in the event of minor mechanical loads. When oxygen is used for inflation, rejects owing to silicon inclusions are greatly reduced. In fact, it has been found that, when sufficiently finely divided, aluminium is oxidized to Al₂O₃, but that, on the other hand, the oxidation of elemental silicon, once formed, is not very probable, as a SiO₂ protective skin is formed during the oxidation, which prevents further oxidation. According to the present invention reduction of silicon oxide takes place to a much lesser extent.

In the process according to the invention, preferably 1-2 Nm³ of oxygen is used per tonne of glass. The quantity of oxygen used per tank furnace is about 10-20 Nm³/hour, which is preferably introduced by means of 10-20 nozzles. More particularly such nozzles are arranged in 2 rows, at least one of which is present in the melting zone of the tank furnace.

Examples I-IV

In the following examples, a number of mixtures are described that can be used according to the present invention.

	I	II	III	IV
sand	398.6 kg	404.9 kg	389.5 kg	330.6 kg
soda	123.9 kg	122.0 kg	125.5 kg	90.9 kg
lime stone	103.7 kg	103.4 kg	62.3 kg	83.8 kg
dolomite	22.0 kg	20.5 kg	-	19.6 kg
phonolite	-	38.6 kg	-	53.5 kg
feldspar	43.2 kg	-	22.2 kg	-
chromium ore	12.4 kg	14.4 kg	7.7 kg	-
chromium oxide	1.2 kg	-	-	3.6 kg
chromium slag	-	-	68.9 kg	-
sodium sulphate	7.2 kg	7.2 kg	10.0 kg	3.0 kg
saltpetre, preferably sodium				
saltpetre	9.0 kg	9.0 kg	5.0 kg	10.0 kg
fragments	400 kg	400 kg	400 kg	500 kg
	1000 kg	1000 kg	1000 kg	1000 kg

The chemical analysis of the glasses made from the above mixtures are, in % by weight, as follows:

	I	II	III	IV
SiO ₂	71.2%	71.0%	71.0%	71.9%
Al ₂ O ₃	1.9%	1.9%	1.9%	2.1%
Fe ₂ O ₃	0.5%	0.7%	0.4%	0.33%
Cr ₂ O ₃	0.75%	0.75%	0.7%	0.4%
CaO	10.4%	10.4%	10.7%	10.4%
MgO	1.3%	1.3%	1.6%	1.3%
Na ₂ O	12.9%	12.9%	13.0%	12.4%
K ₂ O	0.8%	0.8%	0.5%	0.8%
SO ₃	0.2%	0.2%	0.2%	0.2%

The optical transmission, measured in a sample 2 mm thick is, for the above glass compositions, as follows:

		I	II	III	IV
D (2 mm,	500 nm	21.3%	21.3%	22%	33%
5 air)	450 nm	0.3%	1.4%	2%	3%
	400 nm	0%	0%	0%	0%

The so-called dominant wavelength (λ dominant) is 558 nm for all of the above glass compositions.

10 The glass compositions described above were obtained in a tank furnace under the following conditions:

melt yield 151.1 t/d
 content of fragments (calculated on the
 molten glass) 42.03
 15 moisture content (calculated on the
 starting materials including fragments) 2.0%
 oil consumption 745 l/h
 supplementary electrical heating 910 kW
 specific melting capacity 2568 t/m³ d
 20 specific heat consumption (without
 additional electrical heating) 4419 kJ/kg
 specific heat consumption (including
 supplementary electrical heating) 4929 kJ/kg
 oxygen inflation through 12 nozzles into the
 25 melt and into the refinement zone about 12 m³/h.

The above results show that it is possible, using relatively inexpensive starting materials, and using about 40% recycle glass, to achieve better UV absorption values than was possible according to the state of the art. It is in addition apparent that the present process makes it possible to increase the capacity of a tank furnace.

30 As appears from Example III, it is also possible, according to the present invention, in a manner known per se, to replace the proportions of chromium ore or chromium oxide used fully or partially by a chromium oxide-containing waste slag from the electrosteel manufacture. By using this waste slag, which normally can just be disposed of on a dump, it is possible not only to achieve an improvement in melting, but also to reduce the amount of saltpetre necessary to achieve the desired oxidation to about half.

35 In the accompanying Figure, the curves for the percent permeability for wavelengths of between 350 and 650 nm, through a sample 2 mm thick, are shown for the glass compositions of Examples I, II and III, as compared with the corresponding curve for normal green glass. This last sample, however, was 2.5 mm thick.

40 As it clear, the normal green glass transmits a very large portion of the ultraviolet radiation in the range of between 350 and 500 nm, whereas the glass produced in accordance with the present invention exhibits a high absorption in this range.

45 Depending on the desired absorption in this range, the content of hexavalent chromium is at least 0.01% by weight, calculated on the glass, in particular 0.02 to 0.07% by weight. When a proportion of at least 0.04% by weight is used, a very favourable absorption is obtained.

Claims

50 1. A process for making green glass permeable to visible light and highly absorbing to ultraviolet radiation, by treating a melt of a soda-lime glass under oxidizing conditions with a gas, said melt containing chromium compounds and nitrate, characterized by blowing an oxidizing gas into the melt of the glass, which contains at least 0.3% by weight of chromium, calculated as Cr₂O₃ 0.2-2.0% by weight of Na nitrate, no more than 1.5% by weight of Na sulphate, and 15 to 65% by weight of recycle glass.

55 2. A process as claimed in claim 1, characterized by starting from raw materials whose fluorine and/or chloride content is as low as possible.

3. A process as claimed in claim 2, characterized in that the fluorine content in the glass batch is no more than 0.01% by weight, preferably no more than 0.001% by weight.

4. A process as claimed in claim 2 or 3, characterized in that the chloride content in the glass batch is no more than 0.01% by weight, preferably no more than 0.001% by weight.

5. A process as claimed in claims 1-4, characterized by using as the oxidizing gas an oxygen containing at least 50% by volume of molecular oxygen.

5 6. A process as claimed in claim 5; characterized in that the gas contains at least 95% by volume of molecular oxygen.

7. A process as claimed in claims 1-6, characterized by preparing a glass batch having the following composition in kg, calculated on 1000 kg of glass batch

	sand	300-400 kg
10	soda	50-150 kg
	limestone	60-105 kg
	dolomite	0-25 kg
	phonolite	0-40 kg
	feldspar	0-45 kg
15	chromium ore	0-15 kg
	chromium oxide	0-5 kg
	chromium slag	0-70 kg
	sodium sulphate	0-11 kg
	nitrate	4-15 kg
20	fragments	350-586 kg

in which at least one of the proportions of chromium ore, chromium oxide and chromium slag is not zero.

8. A process as claimed in claims 1-7, characterized in that the product glass has the following composition:

25	SiO ₂	70-74 % by weight
	Al ₂ O ₃	1.5-2.5 % by weight
	Fe ₂ O ₃	0.25-0.7 % by weight
	chromium oxide	0.3-0.85 % by weight (as Cr ₂ O ₃)
30	CaO	10-11 % by weight
	MgO	1-2 % by weight
	Na ₂ O	12-14 % by weight
	K ₂ O	0.4-1 % by weight
	SO ₃	0.1-0.3 % by weight.

35 9. A process as claimed in claims 1-8, characterized in that the conditions are chosen so that the glass contains a proportion of at least 0.01% by weight of chromium (VI) oxide.

10. A process as claimed in claim 9, characterized in that the proportion of chromium(VI)oxide is between 0.02 and 0.07% by weight.

40 11. A process as claimed in claims 1-10, characterized in that the chromium oxides are replaced in full or in part by a proportion of no more than 0.2% by weight of nickel oxide.

12. A process as claimed in claims 1-10, characterized by using 1-3 m³ of oxygen per tonne of glass.

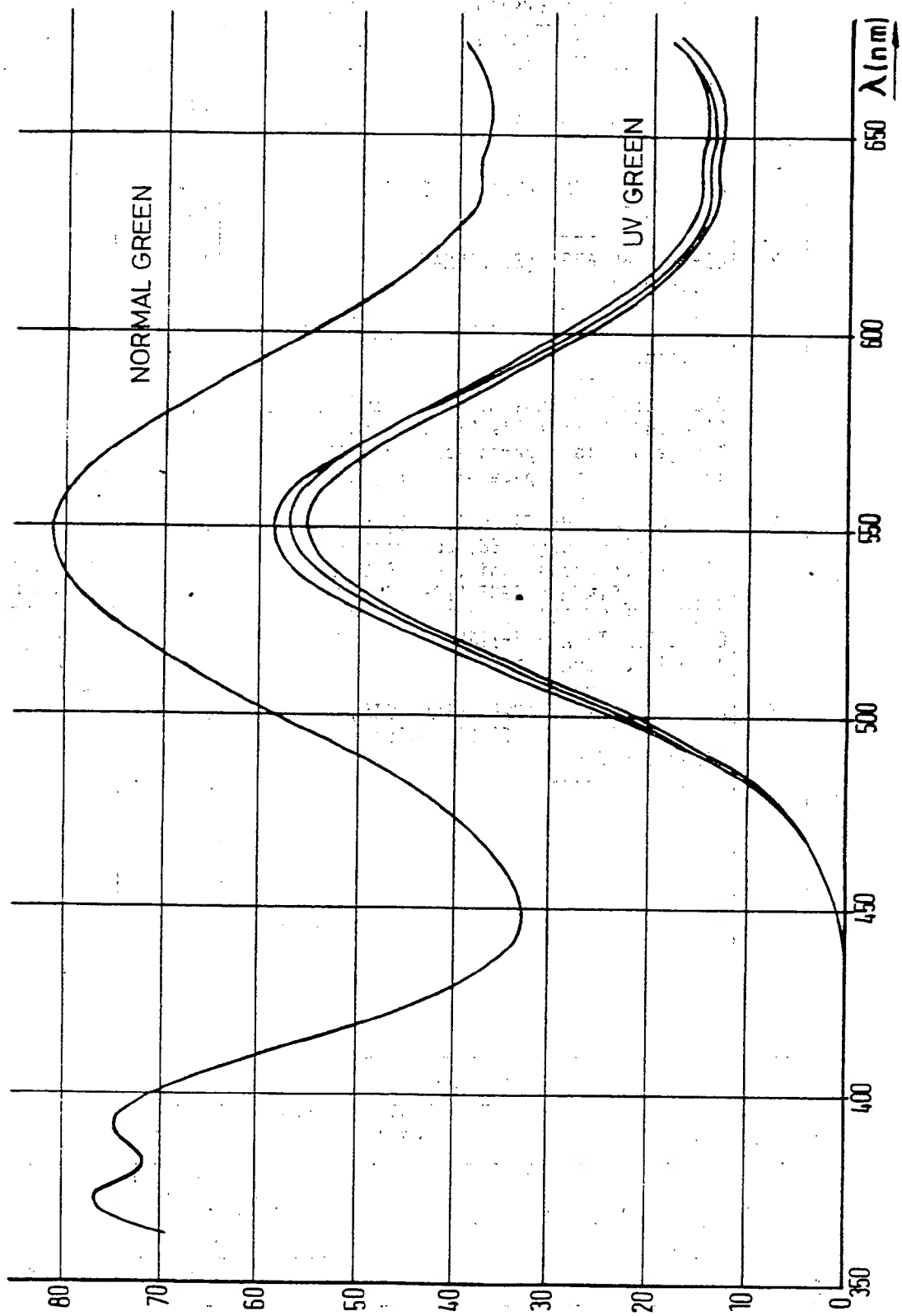
13. A process as claimed in claim 12, characterized in that about 10-20 m³ of oxygen per hour is supplied through 10-20 nozzles.

45 14. A process as claimed in claim 13, characterized in that said nozzles are arranged in two rows, at least one row being positioned in the melting zone of the tank furnace.

15. A container, in particular a bottle, for products sensitive to UV radiation, consisting in full or in part of glass produced in accordance with claims 1-14.

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European Patent
Office

EUROPEAN SEARCH REPORT

Application Number

EP 87 20 1753

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
Y,D	FR-A-1 275 824 (OWENS-ILLINOIS) * Abstract; page 6, left-hand column D, C *	1,5-8, 11-13, 15	C 03 C 4/08 C 03 C 3/087
Y	US-A-2 331 052 (H.A. SHADDUCK) * Claim 1 *	5,6,12, 13	
Y	DD-A-2 69 675 (S. LEHMANN) * Claims *	1,7,8	
Y	GB-A-2 049 656 (THE MOLSON COMPANIES) * Claims *	11	
Y	P.J. DOYLE: "Glass-making today", pages 31,42,43, Portaellis Press, Redhill * Page 31, last paragraph; page 42, last paragraph; page 43, paragraph 1 *	1,7	
Y	CHEMICAL ABSTRACTS, vol. 103, no. 6, August 1985, page 266, abstract no. 41390r, Columbus, Ohio, US; & SU-A-1 151 521 (STATE SCIENTIFIC-RESEARCH INSTITUTE OF GLASS; "KRASNYI LUCH" GLASS PLANT) 23-04-1985 * Whole abstract *	1	
Y	US-A-3 844 796 (OWENS-ILLINOIS) * Column 1, lines 60-68; column 2, lines 39-46 *	1,8,15	
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 08-12-1987	Examiner BOUTRUCHE J.P.E.
<div>CATEGORY OF CITED DOCUMENTS</div> <div>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</div> <div>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons * : member of the same patent family, corresponding document</div>			

1990年12月
 1991年1月
 1991年2月

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[illegible]

The diagram illustrates the experimental setup. A participant is seated at a table, looking at a video screen. On the table, there is a target and a light source. A camera is positioned above the table to capture the movement. The participant's hand is positioned to move the target towards the light source. The video screen displays the target and the light source. The participant is instructed to move the target towards the light source.

[illegible]

the 1990s, the number of people in the United States who are 65 years of age or older has increased by 50 percent, and the number of people 75 years of age or older has increased by 100 percent. The number of people 85 years of age or older has increased by 200 percent. The number of people 95 years of age or older has increased by 400 percent. The number of people 100 years of age or older has increased by 1,000 percent. The number of people 105 years of age or older has increased by 2,000 percent. The number of people 110 years of age or older has increased by 4,000 percent. The number of people 115 years of age or older has increased by 8,000 percent. The number of people 120 years of age or older has increased by 16,000 percent. The number of people 125 years of age or older has increased by 32,000 percent. The number of people 130 years of age or older has increased by 64,000 percent. The number of people 135 years of age or older has increased by 128,000 percent. The number of people 140 years of age or older has increased by 256,000 percent. The number of people 145 years of age or older has increased by 512,000 percent. The number of people 150 years of age or older has increased by 1,024,000 percent. The number of people 155 years of age or older has increased by 2,048,000 percent. The number of people 160 years of age or older has increased by 4,096,000 percent. The number of people 165 years of age or older has increased by 8,192,000 percent. The number of people 170 years of age or older has increased by 16,384,000 percent. The number of people 175 years of age or older has increased by 32,768,000 percent. The number of people 180 years of age or older has increased by 65,536,000 percent. The number of people 185 years of age or older has increased by 131,072,000 percent. The number of people 190 years of age or older has increased by 262,144,000 percent. The number of people 195 years of age or older has increased by 524,288,000 percent. The number of people 200 years of age or older has increased by 1,048,576,000 percent. The number of people 205 years of age or older has increased by 2,097,152,000 percent. The number of people 210 years of age or older has increased by 4,194,304,000 percent. The number of people 215 years of age or older has increased by 8,388,608,000 percent. The number of people 220 years of age or older has increased by 16,777,216,000 percent. The number of people 225 years of age or older has increased by 33,554,432,000 percent. The number of people 230 years of age or older has increased by 67,108,864,000 percent. The number of people 235 years of age or older has increased by 134,217,728,000 percent. The number of people 240 years of age or older has increased by 268,435,456,000 percent. The number of people 245 years of age or older has increased by 536,870,912,000 percent. The number of people 250 years of age or older has increased by 1,073,741,824,000 percent. The number of people 255 years of age or older has increased by 2,147,483,648,000 percent. The number of people 260 years of age or older has increased by 4,294,967,296,000 percent. The number of people 265 years of age or older has increased by 8,589,934,592,000 percent. The number of people 270 years of age or older has increased by 17,179,869,184,000 percent. The number of people 275 years of age or older has increased by 34,359,738,368,000 percent. The number of people 280 years of age or older has increased by 68,719,476,736,000 percent. The number of people 285 years of age or older has increased by 137,438,953,472,000 percent. The number of people 290 years of age or older has increased by 274,877,906,944,000 percent. The number of people 295 years of age or older has increased by 549,755,813,888,000 percent. The number of people 300 years of age or older has increased by 1,099,511,627,776,000 percent. The number of people 305 years of age or older has increased by 2,199,023,255,552,000 percent. The number of people 310 years of age or older has increased by 4,398,046,511,104,000 percent. The number of people 315 years of age or older has increased by 8,796,093,022,208,000 percent. The number of people 320 years of age or older has increased by 17,592,186,044,416,000 percent. The number of people 325 years of age or older has increased by 35,184,372,088,832,000 percent. The number of people 330 years of age or older has increased by 70,368,744,177,664,000 percent. The number of people 335 years of age or older has increased by 140,737,488,355,328,000 percent. The number of people 340 years of age or older has increased by 281,474,976,710,656,000 percent. The number of people 345 years of age or older has increased by 562,949,953,421,312,000 percent. The number of people 350 years of age or older has increased by 1,125,899,906,842,624,000 percent. The number of people 355 years of age or older has increased by 2,251,799,813,685,248,000 percent. The number of people 360 years of age or older has increased by 4,503,599,627,370,496,000 percent. The number of people 365 years of age or older has increased by 9,007,199,254,740,992,000 percent. The number of people 370 years of age or older has increased by 18,014,398,509,481,984,000 percent. The number of people 375 years of age or older has increased by 36,028,797,018,963,968,000 percent. The number of people 380 years of age or older has increased by 72,057,594,037,927,936,000 percent. The number of people 385 years of age or older has increased by 144,115,188,075,855,872,000 percent. The number of people 390 years of age or older has increased by 288,230,376,151,711,744,000 percent. The number of people 395 years of age or older has increased by 576,460,752,303,423,488,000 percent. The number of people 400 years of age or older has increased by 1,152,921,504,606,846,976,000 percent. The number of people 405 years of age or older has increased by 2,305,843,009,213,693,952,000 percent. The number of people 410 years of age or older has increased by 4,611,686,018,427,387,904,000 percent. The number of people 415 years of age or older has increased by 9,223,372,036,854,775,808,000 percent. The number of people 420 years of age or older has increased by 18,446,744,073,709,551,616,000 percent. The number of people 425 years of age or older has increased by 36,893,488,147,419,103,232,000 percent. The number of people 430 years of age or older has increased by 73,786,976,294,838,206,464,000 percent. The number of people 435 years of age or older has increased by 147,573,952,589,676,412,928,000 percent. The number of people 440 years of age or older has increased by 295,147,905,179,352,825,856,000 percent. The number of people 445 years of age or older has increased by 590,295,810,358,705,651,712,000 percent. The number of people 450 years of age or older has increased by 1,180,591,620,717,411,303,424,000 percent. The number of people 455 years of age or older has increased by 2,361,183,241,434,822,606,848,000 percent. The number of people 460 years of age or older has increased by 4,722,366,482,869,645,213,696,000 percent. The number of people 465 years of age or older has increased by 9,444,732,965,739,290,427,392,000 percent. The number of people 470 years of age or older has increased by 18,889,465,931,478,580,854,784,000 percent. The number of people 475 years of age or older has increased by 37,778,931,862,957,161,709,568,000 percent. The number of people 480 years of age or older has increased by 75,557,863,725,914,323,419,136,000 percent. The number of people 485 years of age or older has increased by 151,115,727,451,828,646,838,272,000 percent. The number of people 490 years of age or older has increased by 302,231,454,903,657,293,676,544,000 percent. The number of people 495 years of age or older has increased by 604,462,909,807,314,587,353,088,000 percent. The number of people 500 years of age or older has increased by 1,208,925,819,614,629,174,706,176,000 percent. The number of people 505 years of age or older has increased by 2,417,851,639,229,258,349,412,352,000 percent. The number of people 510 years of age or older has increased by 4,835,703,278,458,516,698,824,704,000 percent. The number of people 515 years of age or older has increased by 9,671,406,556,917,033,397,649,408,000 percent. The number of people 520 years of age or older has increased by 19,342,813,113,834,066,795,298,816,000 percent. The number of people 525 years of age or older has increased by 38,685,626,227,668,133,590,597,632,000 percent. The number of people 530 years of age or older has increased by 77,371,252,455,336,267,181,195,264,000 percent. The number of people 535 years of age or older has increased by 154,742,504,910,672,534,362,390,528,000 percent. The number of people 540 years of age or older has increased by 309,485,009,821,345,068,724,781,056,000 percent. The number of people 545 years of age or older has increased by 618,970,019,642,690,137,449,562,112,000 percent. The number of people 550 years of age or older has increased by 1,237,940,039,285,380,274,899,124,224,000 percent. The number of people 555 years of age or older has increased by 2,475,880,078,570,760,549,798,248,448,000 percent. The number of people 560 years of age or older has increased by 4,951,760,157,141,521,099,596,496,896,000 percent. The number of people 565 years of age or older has increased by 9,903,520,314,283,042,199,193,993,792,000 percent. The number of people 570 years of age or older has increased by 19,807,040,628,566,084,398,387,987,584,000 percent. The number of people 575 years of age or older has